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Trawling for Complements

A method has been invented for determining nanoscale variations in the distribution of electric charge on surfaces. It has so far been used to examine specific inorganic materials, but could find widespread applications in imaging.

J. Marty Gregg & Amit Kumar

Thunderstorms are among nature's most awe-inspiring spectacles. Lightning flashes pierce the gloom causing vast amounts of electrical charges, built up at the base of clouds, to find their way to Earth. Even without flashes, static electricity in the clouds affects the charge distribution on the Earth's surface below. Localized regions of land, and all objects contained within them, become either enriched in or denuded of electrons, producing a localised net charge opposite in sign to that of the clouds directly above. Although most of the cloud base is negative, charge densities vary. As the storm passes overhead, these variations are reflected by complementary charge variations on Earth. To facilitate charge redistribution, electrical currents must flow. So, by monitoring the currents at fixed locations on Earth, variations in the charge densities of the passing storm clouds can be mapped. This is almost exactly what Hong *et al.*¹ have done except, rather than map large-scale electrical storms, they have invented an analogous technique to determine nanoscale charge variations on the surfaces of inorganic functional materials.

To do their experiments, Hong and colleagues made relatively minor adaptations to an atomic force microscope (AFM), if anything simplifying its mode of operation over that conventionally used. They brought a sharp conducting tip, on the end of a flexible cantilever, into contact with the surface of a lithium niobate crystal. They then trawled this metallic tip across the

crystal surface and, using a sensitive detection circuit, monitored minute currents associated with charge redistribution between the tip and its grounded electrode.

Lithium niobate is an insulating oxide, important in telecommunications applications. Within each of the unit cells of this crystalline material, ions are naturally arranged such that the centres of positive and negative charge are slightly spatially separated. This results in what is termed an electrical dipole, a vector entity which points from negative to positive within the crystal. In lithium niobate, the orientation of this dipole can be reversed by an electric field, defining the material as a ferroelectric. For applications, reversals in dipole orientation induced by an electric field are deliberately engineered to make spatially periodic stripe patterns, where positive and negative charges are alternately closest to the crystal surface, in distinct regions called domains. When electrodes are brought into contact, the proximity of the near-surface charges in the ferroelectric induces charge redistribution in the electrode: charges of opposite sign to the near-surface charges in the ferroelectric are attracted to the electrode-ferroelectric interface and like charges are repelled away.

The same thing happens when an AFM tip is used as an electrode (Fig. 1). If this tip is moved within a single domain, because dipoles are uniformly oriented, the initial charge redistribution that occurs in the tip remains unchanged. However, whenever the tip passes over the junction between one domain and the next (over a domain wall), dipole reversal causes complementary charges to flow between the tip and its grounded electrode. Because the current associated with this charge redistribution between the tip and ground is proportional to the rate of change of charge at the tip, it increases as the scanning speed of the AFM tip increases (complete charge redistribution is forced to occur in a shorter time). Moreover, because the nature of the charge redistribution in the tip depends on the sense in which a specific domain wall is traversed, the sign of the current changes whenever the scan direction is reversed. Hong *et al.* point out that the total current that is generated as the tip passes over each domain wall equates to a charge-density change at the ferroelectric surface around twice that of the dipole density in lithium niobate,

exactly as should be expected. Importantly, this confirms that the new technique can quantitatively, as well as qualitatively, map nanoscale charge density variations. Hong *et al.* do highlight the confounding influence of ions or dipolar molecules in the air that nullify the electric fields generated by the near-surface charges in the ferroelectric. However, they note that their novel imaging technique, which they call charge gradient microscopy, is largely immune to such air-borne layers, as it seems that the rastered tip scrapes them away.

While this new methodology for imaging charge variation is conceptually rather simple, its potential importance cannot be overstated. It has recently become evident that ferroelectric domain walls can possess diverse functional characteristics that are completely different from the domains that they delineate: they can be conducting², or even superconducting³, when the domains themselves are insulating. Moreover, they can be moved, injected and annihilated by external electric fields⁴, so that their potential use in ‘active’ two-dimensional electronic devices is overwhelmingly clear. Hong and colleagues’ imaging technique rapidly locates ferroelectric domain walls and could therefore be invaluable in supporting the quest for “domain wall nanoelectronics”⁵. Moreover, its discovery comes at a point when shortcomings in the most common method for ferroelectric domain imaging (piezoresponse force microscopy) are starting to become uncomfortably apparent: for example, high-quality images of ‘domains’ have been obtained using piezoresponse force microscopy in materials in which ferroelectricity is extremely unlikely^{6,7}.

Restricting the authors’ charge gradient microscopy to imaging ferroelectric domain walls, exciting as they are, would probably be a mistake. Variation in nanoscale charge distribution must be crucial in many aspects of science, from understanding communications in cell biology to teasing out details in battery electrochemistry. Perhaps it will be through the adoption of this imaging technique by other areas of science, that its full potential will be realized.

Figure 1 | Charge gradient mapping. Hong and colleagues¹ have developed a technique to determine charge variations on the surfaces of ferroelectric materials. A metallic tip connected via

an electrode to the ground rasters rapidly across the surface of the material, which is also connected to the ground. The tip only records a current in a device equivalent to an ammeter (A) when it encounters a charge gradient at a junction between two distinct domains, in which positive and negative charges are alternately closest to the surface; the black arrows denote the electrical-dipole vectors in each domain. The magnitude of the current (blue and brown curves), which is associated with charge redistribution in the tip (grey curve), is proportional to the charge gradient as well as the tip velocity; its sign is governed by the sense of the charge gradient, as well as the scan direction.

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